

# PATENT SPECIFICATION

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## (54) IMPROVEMENTS RELATING TO THE MANUFACTURE OF MICROCAPSULES

(71) We, AGFA-GEVAERT, a naamloze vennootschap organised under the laws of Belgium; of 27, Septestraat, B 2510 Mortsel, Belgium; do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for forming microcapsules comprising a hydrophilic material in an envelope of a water-insoluble, oleophilic material.

An encapsulation process suitable for that purpose is described in the United Kingdom Patent Specification 1,048,696 filed July 10, 1963 by Gevaert Photo-Production N.V. According to said Patent Specification microcapsules containing aqueous material can be formed by emulsifying such material in a solution of an encapsulating substance in a water-immiscible solvent, emulsifying such emulsion in an aqueous solution of a hydrophilic colloid, and subsequently removing the water-immiscible solvent containing the encapsulating substance e.g. by evaporation. The encapsulating substance that has to form a coherent envelope around the aqueous liquid fill of the microcapsules is preferably a film-forming hydrophobic polymer. The hydrophilic colloid dissolved in the aqueous phase in which the first formed emulsion has been emulsified acts as a protective colloid and dispersing agent for the droplets containing the encapsulating substance surrounding the aqueous liquid fill.

It has been established experimentally that a rather large proportion of the droplets produced according to the process of said United Kingdom Patent Specification 1,048,696 does not consist of droplets having an aqueous liquid fill but rather consists of small spheres entirely consisting of encapsulating substance.

It is one of the objects of the invention to provide an emulsification process ensuring an improved yield of filled microcapsules comprising a hydrophilic phase enveloped by a film-forming oleophilic phase.

According to the present invention a process for the manufacture of microcapsules comprising a hydrophilic liquid in a hydrophobic envelope involves the following steps:

(A) emulsifying a volume  $V_1$  of a hydrophilic liquid in a volume  $V_2$  of a hydrophobic liquid consisting of or containing a substance or substances for forming hydrophobic capsule envelopes, the volume  $V_1$  being not greater than a volume  $X_1$ , where the ratio  $X_1/(X_1 + V_2)$  corresponds with the first inversion point of the emulsion formed and

(B) rapidly adding to such formed emulsion, while agitating or stirring, a volume  $V_3$  of hydrophilic liquid to form an emulsion system comprising a hydrophilic liquid continuous phase and a disperse phase comprising droplets of hydrophilic liquid enveloped in a hydrophobic liquid phase consisting of or containing said envelope-forming substance(s), the volume  $V_3$  being such that  $V_1 + V_3 \geq X_2$ ,  $1/5 (X_2 = X_1)$  where the volume  $X_2$  is such that the ratio  $X_2/(X_2 + V_2)$  corresponds with the second inversion point of the emulsion system and

(C) allowing or causing the said envelope-forming substance(s) in said enveloping hydrophobic liquid phase to form solid envelopes around said droplets.

In the present specification the expression "hydrophilic liquid" is used to denote all aqueous liquids in which water is one of the essential components, and any other hydrophilic liquids that are miscible with water but are not a solvent for the components of the oleophilic liquid.

The expression "oleophilic liquid" includes all liquid compositions of hydrophobic character and relates e.g. to water-immiscible liquids, an oleophilic solution of a hydrophobic film-forming agent or of a liquid or dissolved substance(s) from which such an agent can be formed in situ e.g. by polymerisation, polyaddition or polycondensation and relates likewise to liquid hydrophobic monomers and to molten oleophilic film-forming material e.g. molten wax or molten thermoplastic resin.

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The notion "inversion point" may be defined as the critical volume ratio at which an emulsion at a constant temperature ceases to contain one of the liquid materials entirely in dispersed form in the other or in another liquid material which forms the continuous phase of the emulsion.

The possible emulsification states of a two-component liquid system can be illustrated by a so-called inversion diagram or Ostwald diagram as shown in Figure 1.

In Figure 1 the theoretical inversion diagram (Ostwald diagram) has been represented for an emulsion of an aqueous phase (W) and an oleophilic phase (O). In that diagram a range of volume parts consisting of an aqueous phase is plotted on a first line going from the right to the left from 0% by volume of aqueous liquid (corresponding with 100% by volume of oleophilic liquid) to 100% by volume of aqueous liquid (corresponding with 0% by volume of the oleophilic phase).

As a result of the possibility of transforming an oil-in-water (O/W) type emulsion into a water-in-oil (W/O) type emulsion (and vice versa) by gradually changing the volume parts of the mutually immiscible liquid components and by the fact that in practice the two types of emulsion systems can exist in intermixed state i.e. simultaneously, two inversion points ( $I_1$  and  $I_2$  in the diagram) corresponding with complementary volume ratios are a characteristic of each inversion diagram describing a specific emulsion system of only two mutually non-miscible liquids.

The theoretical inversion points correspond with the maximum volume that can be occupied by spherical droplets of equal diameter of the dispersed phase when said droplets are disposed in a hexagonal packing, each droplet touching twelve neighbouring ones. Such an arrangement is called rhombohedral. The volume occupied by said droplets in such an arrangement stack is 74.2% of the total volume of the system.

Consider the case where a gradually increasing volume of water is added to a volume of oil and suitably agitated to form an emulsion. As the volume of water in the system rises from 0% to 25.8%, that is, range B of Figure 1, the emulsion is exclusively a water in oil emulsion. This volume ratio corresponds to  $I_1$  in the diagram, the first inversion point. When the volume of water exceeds 25.8%, that is, beyond the first inversion point, the system can comprise a mixture of two phases namely a water in oil emulsion phase and an oil in water emulsion phase. This is range C of Figure 1. Water can be added so that the volume of water in the system reaches 74.2% (the volume of oil being 25.8% of the system) which corresponds to the second or complementary inversion point  $I_2$  in Figure 1. Beyond this second or complementary inversion point, the system becomes exclusively an

oil in water emulsion, range A of Figure 1.

Conversely, if a gradually increasing volume of oil is added to water and suitably agitated to form an emulsion,  $I_1$  becomes the first inversion point and  $I_2$  the second or complementary inversion point. Again, in range A the system consists of an oil in water emulsion, in range B of a water in oil emulsion and in range C of a mixture of the two phases.

It will be noted that the present invention relates to the enveloping of an aqueous or hydrophilic phase in a hydrophobic phase so that  $I_1$  and  $I_2$  as marked on Figure 1 correspond to the first and second inversion points respectively. Thus for the purposes of this specification if a volume of  $X_1$  of hydrophilic liquid were added to a volume  $V_1$  of hydrophobic liquid and emulsified the system would be at the first inversion point  $I_1$  and if a volume  $X_2$  of hydrophilic liquid were added to the same volume  $V_1$  of hydrophobic liquid and emulsified, the system would be at the second or complementary inversion point  $I_2$ .

It will be appreciated that Figure 1 and the numerical volume ratios (25.8% and 74.2%) cited above correspond to the theoretical inversion points. In practice it will normally be the case that the dispersed droplets differ in size and this means, because the interstices between the larger droplets can be occupied by smaller ones, that the numerical ratios cited above can differ appreciably. For example, it may be possible for the inversion points to correspond with volume ratios of 10% and 90%.

It has been established experimentally that in order to obtain a very high yield of filled capsules in a  $W_1/O/W_2$  emulsion system it is preferable to start in a first step with the preparation of a  $W_1/O$  emulsion having in range B (see Figure 1) a volume ratio of first hydrophilic liquid ( $W_1$ ) as close as possible to the first inversion point ( $I_1$ ).

In a second step the second hydrophilic liquid ( $W_2$ ) is added rapidly preferably in a period of not longer than 2 seconds and in such an amount that almost immediately the hydrophilic phase volume ratio characteristic for the first inversion point ( $I_1$ ) is passed and the volume of hydrophilic liquid switches from range B to come close to the second inversion point ( $I_2$ ) or ends in range A.

The amount of hydrophilic liquid added in the second step should be such that the second inversion point is almost reached or is exceeded, that is, that the volume ratio actually reached is such that the additional amount of hydrophilic liquid to be added so as to reach such second inversion point (if any) is less than 1/5th and preferably less than 1/10th of the amount of hydrophilic liquid necessary to move from the first inversion point to the second.

It is clear from the preceding that in order to apply the process of the present invention it is necessary to be able to determine the

volume ratios of the immiscible liquids at the said inversion points.

5 In connection herewith it has to be noted, that the volume consisting of the introduced hydrophilic liquid and a specific hydrophobic liquid at the inversion points is among other things dependent on temperature, droplet size distribution, the concentration of emulsifying agent and hydrophilic colloid in the hydrophilic phase and the viscosities of the different phases.

10 The behaviour of each emulsifying agent will be different and depend on the degree and distribution of the hydrophilic and hydrophobic groups in the emulsifying agent molecule presenting the so-called hydrophilic-lipophilic balance of the emulsifying agent.

15 In the present process the composition of the first hydrophilic liquid phase  $W_1$  may be the same as that of the second hydrophilic liquid phase  $W_2$ , but need not be.

20 Bearing this in mind, and bearing also in mind that for a given emulsion system there are two inversion points, we can define the term "inversion point" in relation to an emulsion containing immiscible liquids, one of which is wholly dispersed in the other or in another liquid forming a continuous phase, more particularly as being a critical volume ratio between the immiscible liquids such that at the point when a said ratio is reached during the incorporation into the emulsion of an increasing proportion of said one liquid or during the removal from the emulsion of any quantity of the liquid forming the continuous phase, some of the latter liquid become dispersed in some of said one liquid.

30 The volume of hydrophilic liquid at the second inversion point ( $I_2$ ) can be easily determined by measuring the electrical resistivity or conductivity of the emulsions.

40 Indeed, the electrical resistivity of an emulsion (which by changing the volume ratio of hydrophilic liquid with respect to oleophilic liquid passes from zone B into zone A) decreases abruptly on entering zone A since the non-polar phase (oleophilic phase) becomes then the continuous phase which is considerably less electroconductive than the polar phase (hydrophilic phase) which latter is then present as the dispersed phase.

50 The material for the capsule shells prepared according to the process of the present invention is preferably composed of one or more water-insoluble substances that is or are soluble in a water-immiscible solvent or mixture of such solvents and that has or have, or obtain(s) by evaporating the solvent(s) and/or by hardening or cross-linking, a sufficient cohesion power to form a coherent envelope or film around the hydrophilic liquid fill.

60 In the process according to the invention, practically all preformed, film-forming, hydrophobic polymers which are resistant to water and soluble in a water-immiscible solvent

having a boiling point lower than  $100^\circ\text{C}$ , are suited for forming the capsule wall.

Film-forming substances suited for forming the capsule shell according to the present invention are e.g. of the class of hydrophobic addition polymers formed by polymerisation or copolymerisation of vinyl polymers such as styrene, vinyl chloride, vinylidene chloride, vinyl esters, vinyl ethers, acrylic acid esters and methacrylic acid esters, acrylonitrile and methacrylonitrile.

70 Further suitable hydrophobic polymers that are soluble in a water-immiscible organic solvent can be prepared by polycondensation reaction, such as polyamides and polyester-amides, polycarbonates, e.g. a polycarbonate of 2,2-bis(4-hydroxyphenyl)-propane, polycarboxylic acid esters of polyols or polyphenols, polysulphonates and polyphosphonates. Still further suitable hydrophobic polymers that are soluble in a water-immiscible organic solvent and can be prepared by polyaddition such as the polyurethanes and water insoluble modified natural polymers, are, for example hydrophobic cellulose derivatives, particularly ethylcellulose and hydrophobic chlorinated elastomers, e.g. chlorinated rubber.

80 Information about solvents that are immiscible with water and have a boiling point below  $100^\circ\text{C}$  can be found in the book of C. Marsden: Solvents Manual with Solubility Chart, Elsevier Press Inc., New York (1954). Miscibility or immiscibility data of the most common solvents with water can be found in the tables on pages 1394 to 1401 of D'Ans und Lax, Taschenbuch für Chemiker und Physiker, Springer Verlag, Berlin (1949).

95 In the preparation of the capsules it is sometimes necessary to use anti-foaming agents, e.g. octyl alcohol, during the step of evaporating the organic solvent or mixture of organic solvents. The organic water-immiscible solvent is preferably of such type that it can be easily removed by evaporation under normal pressure conditions, in other words it has preferably a boiling point below  $100^\circ\text{C}$ .

100 Suitable water-immiscible solvents are aliphatic and aromatic water-repellent solvents e.g. hydrocarbons such as n-hexane, benzene, halogenated hydrocarbons, e.g. methylene chloride-chloroform and carbon tetrachloride, and water-immiscible ethers, e.g. diethyl ether.

115 In order to obtain a solid capsule shell these solvents have to be removed. This can be done by gradually evaporating the solvents, with or without operating under reduced pressure. When a monomer is used, which can be polymerized at the right time e.g. photopolymerized or a wax or polymer melt as oleophilic phase, the problem of solvent evaporation does not exist.

120 Hydrophilic colloids or emulsifying agents or dispersing agents that may be used in the first and/or second hydrophilic phase are 130



preferably at least 1%, by weight soluble in water at room temperature. Suitable hydrophilic colloids for that purpose are hydrophilic natural colloids, modified hydrophilic natural colloids, or synthetic hydrophilic colloids, for example hydrophilic colloids such as gelatin, glue, casein, zein, hydroxyethylcellulose, carboxymethylcellulose, methylcellulose, carboxymethyl-hydroxyethyl-cellulose, gum arabic, sodium alginate, polyvinyl alcohol, poly-N-vinylpyrrolidone, polyvinylamine, polyethylene oxide, polystyrene sulphonic acid, polyacrylic acid, polymethacrylic acid and hydrophilic copolymers and derivatives of such polymers. Among these colloids gelatin is preferably used. Especially good results are obtained with polyvinyl alcohol and polystyrene sulphonic acid. For other dispersing agents reference is made to the so-called "Tensiden" described by H. König in Zeitschr. Anal. Ch. 251, 127-129.

The liquid to be encapsulated may contain ionic and/or non-ionic substances but should not necessarily contain only dissolved substances; it may contain dispersed particles or substances, e.g. suspended compounds such as colloidal silica and other colloidal particles and pigments.

According to a preferred embodiment, when the composition of the first hydrophilic liquid phase ( $W_1$ ) differs from that of the second hydrophilic liquid ( $W_2$ ) it is advantageous to operate with a first hydrophilic phase ( $W_1$ ) the viscosity of which is greater than that of the second such phase ( $W_2$ ).

According to a further preferred embodiment the temperature of the emulsion during its preparation step (A) is kept as nearly constant as possible in order to avoid fluctuations with respect to the  $W_1/O$  inversion point.

The liquid of the fill of the capsules may for example be wetting agents, hygroscopic compounds e.g. glycerol, fluorescing compounds, compounds decreasing or increasing the pH (pH controlling compound), fertilizers, phytopharmaceuticals, plant growth hormones, vitamins, pharmaceuticals, dyes, all types of chemically reactive compounds, e.g. reducing agents, oxidizing agents, hardening agents, polymer cross-linking agents, colour reactants e.g. leuco dyes or catalysts, which have to be kept apart from (a) reactant(s) or co-reactant(s) till the moment of dissolution, degradation, melting or rupture of the capsule shells.

When the capsule is exposed to normal atmospheric circumstances, encapsulated water will remain encased for a period of time determined by the water-permeability of the capsule wall. However, the substances dissolved or emulsified in the water will remain encased indefinitely. Substances causing water to remain encased e.g. glycerol may be added either to a hydrophilic phase or to the oleophilic phase.

The capsules prepared according to the present invention can be applied in a recording system wherein capsules are ruptured by an applied pressure, and form the basic ingredient for a carbonless duplicating material.

So, in pressure-sensitive materials capsules may be used that can be ruptured by pressure and that contain (a) reactant(s), e.g. a colour coupler for (a) co-reactant(s) present in the recording sheet itself or in a receiving material wherein they can be transferred, e.g. by diffusion or evaporation.

The capsules may likewise find application in photo-sensitive recording systems or materials. For example ingredients suitable for use in photographic processing can be encapsulated and set free at the proper moment in photographic processing by melting or rupturing the capsule shells. So, it is possible e.g. to incorporate a stabilizing agent in encapsulating form into a gelatin-containing layer of a silver halide photographic material, and to set it free at the proper moment, e.g. by capsule rupture or melting.

Further in connection with photographic materials the encapsulating technique may be used for preparing so-called packet emulsions containing light-sensitive silver halide, and for encapsulating one or more photographic ingredients e.g. hydroquinone and other known silver halide developing agents, hardening agents for photographic colloids such as gelatin, fixing agents, e.g. compounds yielding thiosulphate ions, image-stabilizing agents, e.g. compounds yielding isothiocyanate ions, development-activating or development-retarding substances, e.g. compounds increasing the pH, bleaching agents for silver or dyes, colour couplers, dyes, physical developing agents such as compositions comprising a water-soluble noble metal salt, e.g. silver nitrate and/or (a) reducing agent(s) in admixture with e.g. developing agents, such as hydroquinone and 1-phenyl-3-pyrazolidinone.

The capsules may likewise contain diazo compounds and/or couplers for use in diazo-type recording. Capsules prepared according to the present invention may further find use as toner particles in the development of electro-photographic materials.

In thermographic materials capsules prepared as described herein and having a melt-able capsule shell may be used. Such capsules contain e.g. (a) reactant(s) e.g. (a) colour coupler(s), which is (are) set free from the capsules upon melting of the capsule shell and is (are) allowed to react with (a) reactant(s) being or brought into intimate contact with the freed capsule content.

The present invention is illustrated by the following examples without, however, being limited thereto.

The percentages and ratios are by weight unless otherwise indicated.

### Example 1

#### 1. The starting solutions

— 200 ml of a 10% by volume solution in distilled water of sulphonated castor oil, hereinafter called hydrophilic phase (W) were prepared.

— 100 ml of a 10% solution in methylene chloride of the copolymer of vinyltoluene and isobutylmethacrylate (53/47) hereinafter called hydrophobic phase (O) were prepared.

#### 2. Comparison of emulsification procedures

Before operating along the lines of the emulsification procedure of the present invention emulsions with different volume parts of hydrophilic phase were prepared to effect thereon a conductivity measurement. The measurement was performed using a Wheatstone bridge type apparatus. By this technique it was possible to determine the second inversion point  $I_2$  as represented in the graph of Figure 2 in which the resistivity (R) expressed in Ohms is represented as a function of the volume of aqueous liquid (W) in the emulsion system. This inversion point corresponded at 25°C with a hydrophilic phase of 67% of the total volume. In other words when taking 100 ml of the above defined hydrophilic phase (O) we need at the second inversion point ( $I_2$ ) 200 ml of the hydrophilic phase (W) to form an emulsion of droplets of polymer solution surrounded by a continuous medium of the hydrophilic phase.

In order to obtain a maximum yield of hydrophilic-phase-filled microcapsules in a W/O/W system the operating conditions have to be chosen in such a way that first a W/O emulsion is prepared in which the volume of hydrophilic phase does not exceed the so-called first inversion point ( $I_1$ ) at which 33% of the total volume consists of the hydrophilic solution of sulphonated castor oil and that from this emulsion the second inversion point ( $I_2$ ) is reached very quickly.

For comparison's sake three different emulsification procedures A, B, and C were tested. Their results at different rates of liquid addition are listed in the accompanying Table.

A. The whole hydrophilic phase (W) of 200 ml of said aqueous sulphonated castor oil solution was added to the 100 ml of hydrophobic phase (O) while stirring the liquids to be emulsified with a VIBRO-MISCHER (Trade Mark) (a mixing apparatus of CHEMAP A. G. Switzerland).

The rate of addition was different for the tests  $A_1$  and  $A_2$ , see the Table.

B. The hydrophilic phase (W) having a

total volume of 200 ml was added in two separate portions to 100 ml of hydrophobic phase (O). The first part of the hydrophilic phase was added at the rate indicated in the Table in an amount of 50 ml so that the first inversion point ( $I_1$ ) characterized by 33% of aqueous sulphonated castor oil phase in the total volume was not surpassed. During this addition mixing was effected by the already mentioned VIBRO-MISCHER.

Thereupon at the rate indicated in the Table and with continuous stirring, the second part of the hydrophilic phase (150 ml) was added so that substantially the second inversion point ( $I_2$ ) was attained.

C. A water-in-oil type emulsion was prepared by mixing a first portion of the hydrophilic phase (50 ml) in the hydrophobic phase (100 ml) so that the first inversion point ( $I_1$ ) was not surpassed. The obtained emulsion was then added to the second portion (150 ml) of the hydrophilic phase so that substantially the second inversion point ( $I_2$ ) was attained.

After terminating the addition stage in the above three tests the obtained emulsions were kept stirred with the VIBRO-MISCHER for 60 seconds at the same temperature (25°C). This additional mixing resulted in a smaller droplet size distribution.

The obtained emulsions were kept on a water-bath at 40°C for 16 h with gentle stirring by means of a blade stirrer in order to remove the methylene chloride and to have the polymeric capsule envelopes solidified.

The capsules obtained were separated by suction from the hydrophilic phase and dried at room temperature.

From the following Table it clearly appears that the test  $B_1$  carried out according to the emulsification procedure of the present invention offers the best results.

In said Table we find for each test the rate of addition of the defined liquids and the data relating to: ~

1) the capsule size range (S.R.) i.e. the size range comprised between the size of the smallest and largest capsules expressed in microns

2) the yield (Y) of filled capsules, expressed in percent, obtained by the following equation:

$$\frac{C \times 100}{(C + P)} = Y$$

wherein:

C is the amount of filled capsules, and  
P is the amount of pure polymer spheres.

TABLE

Test	Sequence of addition	Rate of addition (sec)	S.R (μ)	Y (%)
A <sub>1</sub>	100 ml (O) + 200 ml (W)	45	0.1-4.1	32
A <sub>2</sub>	100 ml (O) + 200 ml (W)	1	3.4-61.5	12
B <sub>1</sub>	100 ml (O) + 50 ml (W) + 150 ml (W)	45 1	0.1-68.4	77.5
B <sub>2</sub>	100 ml (O) + 50 ml (W) + 150 ml (W)	1 45	3.4-37.6	12
C <sub>1</sub>	[100 ml (O) + 50 ml (W)] added to 150 ml (W)	45 108	0.1-48	34
C <sub>2</sub>	[100 ml (O) + 50 ml (W)] added to 150 ml (W)	45 2	3.4-51.3	39
C <sub>3</sub>	[100 ml (O) + 50 ml (W)] added to 150 ml (W)	1 2	3.4-27.4	30
C <sub>4</sub>	[100 ml (O) + 50 ml (W)] added to 150 ml (W)	1 105	3.4-30.8	30

**Example 2**

100 ml of a gelatino-silver chlorobromide (10 mole % of bromide) emulsion containing an amount of silver halide equivalent to 56 g of silver per kg were thoroughly mixed by means of a VIBRO-MISCHER with 100 ml of a 100% solution in methylene chloride of polystyrene to form a W/O emulsion. The first inversion point was not surpassed.

With continuous stirring 60 ml of a 0.05% aqueous solution of saponin was added in 2 sec. to the obtained W/O emulsion, thus attaining the second inversion point. The intensive stirring was continued for 1 minute and in order to increase the total volume of the W/O/W emulsion obtained a further 60 ml of the 0.05% aqueous saponin solution were added.

In order to evaporate the methylene chloride the whole composition was then heated slowly on a water bath at 40°C and kept at this temperature for 16 h while effecting a moderate stirring with a blade stirrer.

The obtained mass of capsules consisting of silver halide emulsion droplets surrounded by a solid polystyrene shell was diluted with 5 l of a 0.05% aqueous solution of saponin in order to facilitate the separation by suction.

Finally the separated capsules were washed with 1 l of a 0.05% aqueous solution of

saponin in order to improve the redispersing in water.

The capsule yield was 90%. The amount of encapsulated silver halide expressed with respect to 1 g of capsules corresponded with 30 mg of silver.

**Example 3**

Example 2 was repeated with the difference that the silver halide was encapsulated together with a developing agent. Before starting the emulsification procedure 1 g of 1-phenylpyrazolidin-3-one dissolved in 20 ml of ethanol was added to the said 100 ml of the gelatino-silver chlorobromide emulsion.

**Example 4**

For thermodevelopable silver halide recording materials of the type described in the Belgian Patent Specification 776,583 filed December 13, 1971 by Agfa-Gevaert N.V. it is advantageous to encapsulate the stabilizing agent in a meltable polymer shell so that it is set free only at the moment of the thermal development.

The stabilizing agent elected here for that purpose is hydroxyethylthiourea.

**— Encapsulating procedure**

80 ml of a 10% solution of hydroxy-



ethylthiourea in a 3.3% aqueous gelatin solution was emulsified by means of a VIBRO-MISCHER in 100 ml of a 17% solution in methylene chloride of the copolymer of vinyltoluene and isobutylmethacrylate (53/47). Hereby the first inversion point has not been surpassed.

When in but one sec. 150 ml of a 10% aqueous hydroxyethylurea solution containing 0.1% saponin was added, the second inversion point was attained. During the whole operation the stirring with the VIBRO-MISCHER was continued.

The methylene chloride contained in the W/O/W emulsion obtained was then evaporated slowly by keeping the composition for 16 h on a water-bath of 40°C while moderately stirring.

The obtained capsules were separated by suction and washed with a 0.1% aqueous solution of saponin in order to facilitate their redispersing in water.

Capsule yield: 85%.

The amount of encapsulated hydroxyethylthiourea with respect to 1 g of capsules was 100 mg.

#### WHAT WE CLAIM IS:—

1. A process of preparing microcapsules comprising a hydrophilic liquid in a hydrophobic envelope, which process involves the following steps:

(A) emulsifying a volume  $V_1$  of a first hydrophilic liquid in a volume  $V_2$  of a hydrophobic liquid consisting of or containing a substance or substances for forming hydrophobic capsule envelopes, the volume  $V_1$  being not greater than a volume  $X_1$ , where the ratio  $X_1/(X_1 + V_2)$  corresponds with the first inversion point of the formed emulsion and

(B) rapidly adding to the thus formed emulsion, while agitating or stirring, a volume  $V_3$  of a second hydrophilic liquid to form an emulsion system comprising a hydrophilic liquid continuous phase and a disperse phase comprising droplets of hydrophilic liquid enveloped in a hydrophobic liquid phase consisting of or containing said envelope-forming substance(s), the volume  $V_3$  being such that  $V_1 + V_3 \geq X_2 - 1/5 (X_2 - X_1)$  where the volume  $X_2$  is such that the ratio  $X_2/(X_2 + V_2)$  corresponds with the second inversion point of the emulsion system, and

(C) allowing or causing the said envelope-forming substance(s) in said enveloping hydrophobic liquid phase to form solid envelopes around said droplets,

such envelope forming substance(s) being composed of at least one water-insoluble substance which is or are soluble in a water-immiscible solvent or mixture of such solvents and that has or have, or obtain(s) by evaporating the solvent(s) and/or by hardening or cross-linking, a sufficient cohesion power to form a coherent envelope around the hydrophilic liquid fill.

2. A process of preparing microcapsules according to claim 1, wherein after step B the stirring agitating is maintained for a period of time in which the diameter of the droplets becomes smaller and the size distribution range of the droplets smaller.

3. A process according to either of claims 1 and 2, wherein the addition of the second hydrophilic liquid is performed in a period no longer than 2 seconds.

4. A process according to any one of claims 1 to 3, wherein the temperature of the emulsion during its preparation step (A) is kept constant.

5. A process according to any one of claims 1 to 4, wherein the viscosity of the first hydrophilic liquid phase ( $W_1$ ) differs from the viscosity of the second hydrophilic liquid phase ( $W_2$ ).

6. A process according to claim 5, wherein the viscosity of the first hydrophilic phase ( $W_1$ ) is higher than that of the second hydrophilic liquid phase ( $W_2$ ).

7. A process according to any one of the claims 1 to 4, wherein the compositions of the two hydrophilic liquids are identical.

8. A process according to any one of claims 1 to 7, wherein the film-forming material for forming the capsule envelopes is a hydrophobic addition polymer formed by polymerisation or copolymerisation of vinyl polymers such as styrene, vinyl chloride, vinylidene chloride, vinyl esters, vinyl ethers, acrylic acid esters and methacrylic acid esters, acrylonitrile and methacrylonitrile, a hydrophobic polycondensation or poly-addition polymer which is soluble in a water-immiscible organic solvent or a water-insoluble modified natural polymer.

9. A process according to any one of claims 1 to 8, wherein the capsule shell is solidified by evaporating the solvent(s) for the capsule building film-forming material.

10. A process according to claim 10, wherein an anti-frothing agent is present during the step of evaporation.

11. A process according to any one of claims 1 to 10, wherein the capsule shell forming material is dissolved in an organic water-immiscible solvent or mixture of solvents having a boiling point below 100°C.

12. A process according to any one of the preceding claims, wherein the first and/or second hydrophilic liquid contains a hydrophilic colloid.

13. A process according to any one of the preceding claims, wherein the first and/or second hydrophilic liquid contains an emulsifying agent.

14. A process according to any one of the preceding claims, wherein the hydrophilic liquid of the fill of the capsules contains one or more wetting agents, hygroscopic compounds, fluorescing compounds, compounds decreasing or increasing the pH, fertilizers, phytopharmaceuticals, plant growth hormones,

vitamins, pharmaceuticals, dyes, catalysts, reducing agents, oxidizing agents, polymer cross-linking agents or colour reactants.

5 15. A process according to any one of claims 1 to 13, wherein the capsule fill contains ingredients suitable for use in photo-sensitive recording systems or materials.

10 16. A process according to claim 15, wherein the capsule fill contains one or more silver halide developing agents, photo-sensitive halides, compounds acting as stabilising or fixing agent for photo-sensitive silver halide, development activating compounds, development retarding substances, colour couplers,

15 dyes, bleaching agents for silver or dyes or

hardening agents for photographic colloids.

17. A process according to any one of the preceding claims, wherein the volume  $V_2$  is such that  $V_1 + V_2 > X_2 - \frac{1}{10}(X_2 - X_1)$ .

18. A process according to claim 17, where- 20 in the volume  $V_2$  is such that  $V_1 + V_2 > X_2$ .

19. A process according to claim 1 and substantially as herein described.

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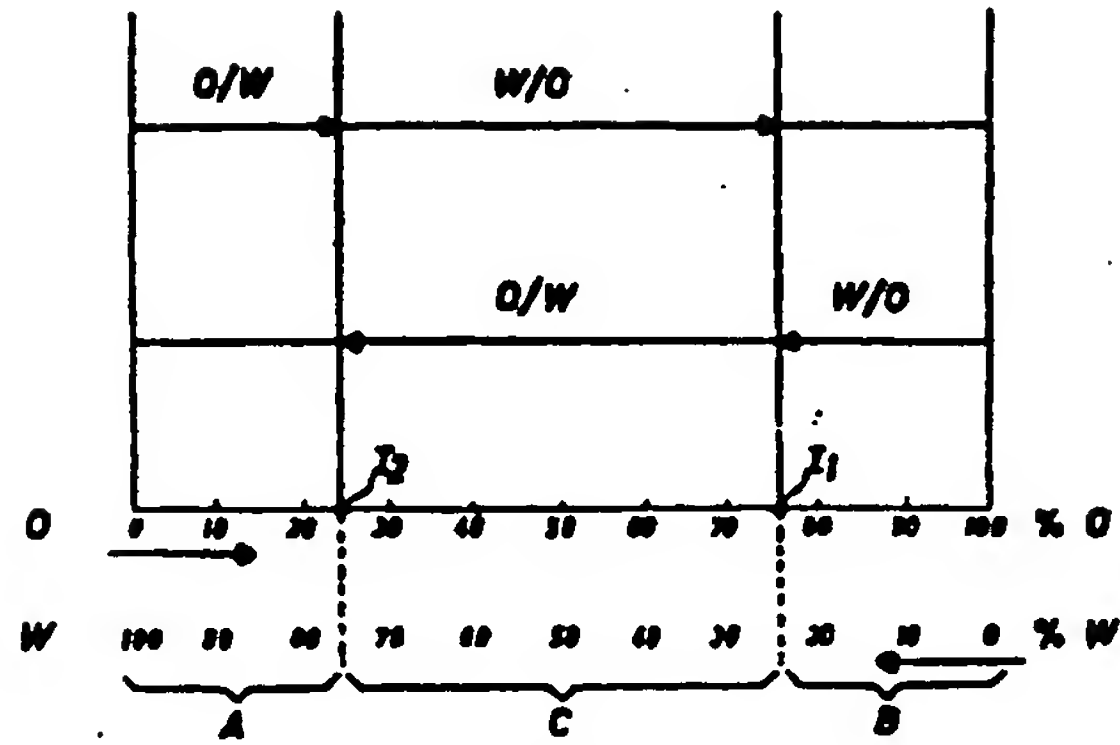


Fig. 1

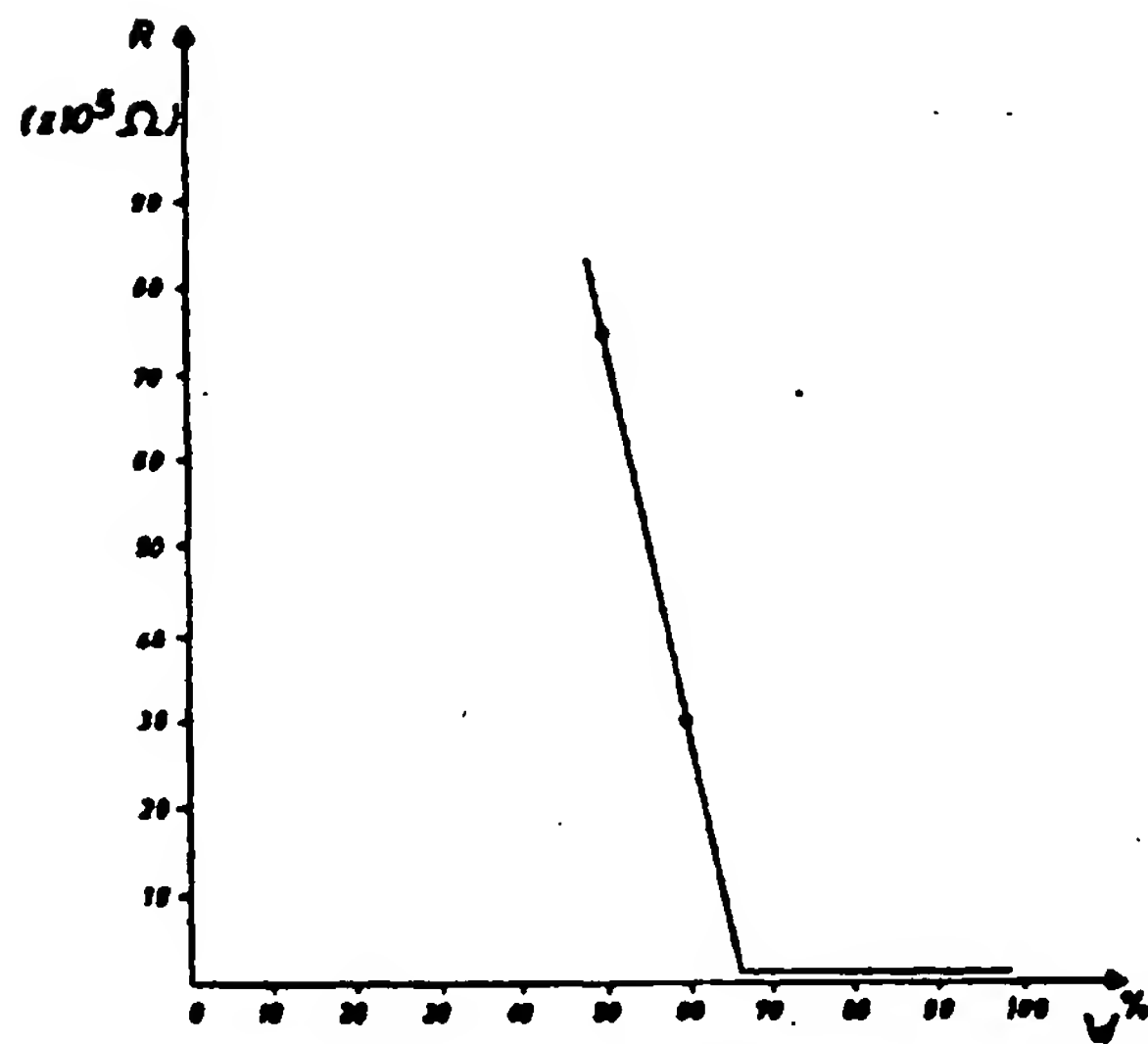


Fig. 2